[redacted]

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
25 October 2001 (25.10.2001)

PCT

(10) International Publication Number
WO 01/79583 A2

(51) International Patent Classification[7]: C23C 14/48, C04B 41/00

(21) International Application Number: PCT/US01/12241

(22) International Filing Date: 13 April 2001 (13.04.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/550,222 14 April 2000 (14.04.2000) US

(71) Applicant *(for all designated States except US)*: TECHNOLOGY INTERNATIONAL, INC. [US/US]; Radtke, Robert, 2103 River Falls Drive, Kingwood, TX 77339-3154 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: RADTKE, Robert [US/US]; 2103 River Falls Drive, Kingwood, TX 77339-3154 (US). TREGLIO, James, R. [US/US]; 12202 Spruce Grove Place, San Diego, CA 92131-2215 (US).

(74) Agent: PARKHURST, Todd, S.; Holland & Knight LLP, 55 West Monroe Street, Suite 800, Chicago, IL 60603-5004 (US).

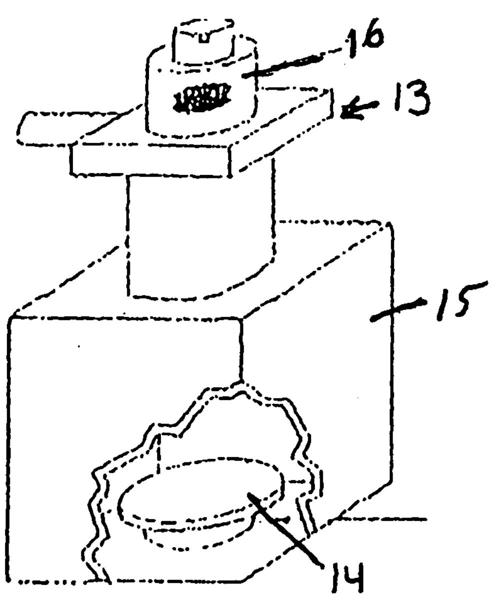
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DIAMONDS AND DIAMOND CUTTERS HAVING IMPROVED DURABILITY



(57) Abstract: The present invention is directed to a process or method of improving the durability of a diamond-type tool, such as a diamond cutter, by providing the diamond-type tool and treating the surfaces of the diamond-type tool to increase the impact strength and fracture toughness. This treatment is by implanting ions into the surface of the diamond-type tool.

WO 01/79583 A2

SPECIFICATION

TITLE

"DIAMONDS AND DIAMOND CUTTERS HAVING IMPROVED DURABILITY"

BACKGROUND OF THE INVENTION

The present invention is directed to a diamond tool and diamond cutter having an improved durability and to the process for providing the improved mechanical properties.

Diamond types include natural diamonds, which are either single crystal or polycrystalline; synthetic polycrystalline diamond compacts commonly called PDC; synthetic polycrystalline composite diamonds commonly referred to as PCD; synthetic thermally-stable diamond compacts commonly referred to as TSP; plasma vapor-deposited diamonds commonly referred to as PVD; and chemically vapor-deposited diamonds. In addition, cubic-boron nitride, which is a diamond-like material and is called CBN, can also be used for a cutter in some instances. Cubic carbon nitride known as CN forms a diamond-like coating for cutting tools. Diamond types have different shapes and sizes naturally occurring and engineered for specific applications. Diamond types include those incorporated in drill bits and machine tools as cutters. Cutters often have substrates which provide a rigid support structure. When attached to a substrate, the diamond portion is called a diamond table. The cutting tip is the portion of the diamond table which engages the workpiece. The workpiece can be a variety of materials including metals, intermetallics, ceramics, fiberglass and rock. Preferably, the substrate includes molybdenum, cobalt-bonded tungsten carbide, a tungsten carbide-copper alloy composite matrix or tool steel. The polycrystalline composite diamond PCD and the polycrystalline diamond compacts PDC are compacts with the diamond table sintered to the cobalt-bonded tungsten carbide in situ during the manufacturing process. The other types of diamonds are attached to substrates by either in situ sintering during their manufacturing, brazing or mechanical attachment methods.

Cutters formed with diamonds are often attached to a diamond tool, such as a drill bit head or machine tool holders and a diamond tool may be a wire drawing die attached to a holder. Durability is a measure of the life of the cutter and is measured, in part, by impact strength, fracture toughness and abrasive wear resistance due to impact cutting. Mechanical tests measure the impact energy, which relates to the impact strength and fracture toughness. Fracture toughness is measured by the amount of energy required to propagate a crack or flaw in the cutter. High impact strength fracture toughness and abrasive resistance are, of course, desirable. However, it is often the case that diamond types of cutters have a low or moderate impact strength and moderate to high abrasive resistance.

Natural diamonds are used in hard rock drilling and in medical tools. Polycrystalline diamond compacts are used as cutters for petroleum and mining rock drilling. The TSP is used for medium-hard rock drilling and wire drawing die materials. The PCD, PVD, CVD and CBN cutters are used for machining abrasive materials, such as fiberglass and silicon-reinforced aluminum. PVD and CVD diamond coatings and cubic CN coatings are applied to tungsten carbide and other machine tools to increase abrasive wear resistance.

Since the introduction of PCD and CBN machine tool cutters in early 1970's and the PDC rock drilling products in the mid-1970's, improvements have been made through design and process improvements. The PCD machine tool uses a fine-grain diamond-type with a high wear resistance and moderate impact strength/fracture toughness. PDC cutters with a larger grain size have a somewhat greater impact strength and fracture toughness and moderate abrasive wear resistance. The toughness in both diamond types is associated with the presence of cobalt. TSP diamonds are made in different chemistries. One brand of TSP is a relatively pure diamond with no cobalt but has porosity as a result of removing cobalt by acid leeching after the process of forming the diamond. Other forms are made with silicon, which also imparts a degree of thermal stability when compared to a PDC with cobalt. TSP, PVD, CVD, CBN, and cubic CN with no cobalt have low impact strength, but have a greater high-temperature wear resistance than a PDC cutter.

Drilling hard rock and abrasive rock and dealing with high-temperature gradients while boring a well have been problems that persist in the well drilling industry. At this time, drill bits using conventional polycrystalline diamond composites (PDC) cutters are unable to sustain a sufficiently high abrasive resistance and resulting bit life at the cutter high temperature associated with drilling hard and abrasive rock, where the drill bit temperature can reach 900°C. PDC abrasive wear rates increase exponentially when a cutting tip temperature exceeds 350°C. Various grades of PDC material are produced by several manufacturers. These grades are tailored to provide the best combination of physical property for each application. One consideration of significance to this invention is that the grain size may be varied from a small grain size of 5μm average particle size to a medium size of 25μm to a high or large size of 50μm, which changes the performance. Within these grain size variations is the ability to vary the diamond table density by the use of diamond powder distribution of mixed sizes where the smaller diamond particles are provided to fill the gaps between the larger diamond particles. Denser diamond tables have an increased abrasive resistance. Generally, small grain size distribution results in high abrasive resistance and low impact strength.

Thermally stable polycrystalline known as TSP diamond cutters have relatively high abrasive resistance at temperatures that reach 1200°C. The current state of the art diamond cutter attachment procedure is to furnace heat, resistance heat or induction braze the TSP diamonds to cobalt-bonded, fine-grain tungsten carbide substrates by means of a suitable brazing filler metal composition. Average shear strength levels of 138MPa to 207MPa, which is 20,000-35,000psi have been achieved using conventional direct resistance, induction and furnace heating methods. However, because of stresses developed in the diamond table due to the difference of the coefficient of thermal expansion between the diamond and the tungsten carbide, the diamond tables can crack on cool-down. This, thus, increases the cost of preparing such cutters.

A major problem in developing an improved cutter is that the PDC conventional cutters cannot be used when the cutter temperature exceeds 350°C due to the high abrasive wear

rate. At about 750°C, the PDC cutters fail altogether. In comparison, a TSP diamond will graphitize and loose both strength and abrasive resistance if it is heated to more than 1200°C. In addition, a further limitation with TSP is the brittle nature of the material.

SUMMARY OF THE INVENTION

An object of the present invention is to provide diamond types and cutters of superior durability due to improved mechanical properties which are caused by a treatment of the diamond type.

These objects are obtained in a diamond-type tool, such as a diamond-type cutter which has means for increasing the impact strength and fracture toughness of the diamond cutter. This means is by implantation of ions into the surface of the diamond member or cutter.

The object can also be obtained by relieving stresses by utilizing a microwave stress relief of the synthetic polycrystalline diamond types, diamond PVD and CVD coatings, naturally occurring diamonds, synthetic diamond grit, cubic boron nitride and cubic carbon nitride coatings.

Before treating the tool to improve the durability, it is subjected to a testing to determine any flaws or cracks. This is by inducing stresses by rapid microwave heating and cooling.

The present inventions is also directed to a process or method of improving the durability of a diamond-type tool, such as a diamond cutter, by providing the diamond-type tool and treating the surfaces of the diamond-type tool to increase the impact strength and fracture toughness. This treatment is by implanting ions into the surface of the diamond-type tool.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a perspective view of an improved diamond cutter in accordance with the present invention;

Fig. 2 is a schematic illustration of a direct ion implantation system with cathode arc ion sources; and

Fig. 3 is a graph showing impact force versus time for different samples.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The principles of the present invention are particulary useful when incorporated in a PDC diamond cutter, generally indicated at 10 in Fig. 1. The diamond cutter 10 has a diamond table 11 which has been sintered to a cobalt-bonded tungsten carbide substrate or base 12 by a known method. The cutter or tool 10 has been placed in an ion implantation reactor, generally indicated at 13 in Fig. 2, and subjected to an ion implantation which penetrates the surfaces of the diamond table in a range of depths of 0.02μm to 0.2μm, with the preferred depth being 0.1μm. This ion implantation does not change the structural shape of the tool and, therefore, a tool which has been subjected to the ion implantation is visually indistinguishable from that of a tool which has not been subjected to ion implantation.

The reactor 13 has a stage 14 on which the tool to be implanted is placed. The stage is in a chamber 15, which is connected to an ion source 16, which is a metal target on a cathode.

The ions are selected from a group consisting of aluminum (Al^{3+}), argon (Ar^{+}), boron (B^{3+}), carbon (C^{4+}), calcium (Ca^{2+}), chromium (Cr^{3+}), hydrogen (H^{+}), nitrogen (N^{5+}), nickel (Ni^{2+}), oxygen (O^{+}), ruthenium (Ru^{4+}), silicon (Si^{4+}), tantalum (Ta^{5+}), titanium (Ti^{2+}), yttrium (Y^{3+}), zirconium (Zr^{4+}) and combinations thereof. The preferred metal ions are titanium, chromium, nickel, yttrium, ruthenium and tantalum. The implant dosage for the ions should be

in a range of 3 x 10^{16} ions/cm^2 to 10^{17} ions/cm^2. Also, it should be noted that during the ion bombardment, the temperature remains below 150°C.

The sizes and the mass of the implanted ions have a significant effect on the properties of the implanted material and increased impact energy (fracture toughness) of each diamond type and grain size distribution is obtained.

It is well-known that the hardness of a material is analogous of the strength measured by the tensile test. Impact energy, which is the energy necessary to fracture a standard test piece under an impact load, is similar analog of toughness. The higher the toughness of the material the higher the impact energy. Therefore, by improving the fracture toughness of a diamond through ion implantation, its impact energy required to fracture the material can be increased. For example a cutter with small grain size of 5μm which has high abrasive resistance will have increased impact strength due to the ion implantation.

From GE Superabrasives, a series of diamond tools were obtained. These tools included a Type 1308 PDC diamond cutters and a Type 2167 TSP diamonds. These tools were taken to Cutting Edge Products, Inc. in San Diego, California, where they were placed in an ion implantation reactor, such as illustrated schematically in Fig. 2, and were subjected to an ion implantation using standard energy for implantation. The reactor had both a titanium and nickel target material and the chamber, after placing the samples therein, was evacuated. The dosage was 10^{17} ions/cm^2.

The TSP diamonds have a 13mm diameter and have a diamond structure without cobalt. The diamond samples that had the ion implantation required at least 30% higher impact energy to fracture, compared to the diamond samples without any implantation. The thicknesses of these samples were recorded and the impact energy required to break the samples was measured using an Instron Instrument Drop Weight Tester. The impact energy was calculated as the integral of the area below the force versus time curves shown in Fig. 3. The curves 21 and

22 are for samples of two different thicknesses of a TSP diamond which had not been subjected to the ion implantation, while curves 3 and 4 are for those TSP diamonds which had ion implantation with Ni^{2+} and Ti^{2+} at an implant dosage of 10^{17} ions/cm^2. The curve 21 is for a TSP diamond having a thickness of 1.8mm, while the curve 22 is for a TSP diamond having a thickness of 2.1mm. The curves 23 and 24 are for two TSP diamond samples which were subjected to the same ion implantation and have a thickness of 2.1mm. As illustrated by the curves 23 and 24, while slightly different, have a greater impact energy for the implanted samples, which energy will relate to a greater fracture toughness created by the selection of the ion implantation process.

Several of the purchased PDC diamond cutters, which have a 13mm diameter and are a diamond structure with cobalt, were also subjected to the ion implantation along with the TSP material. These implant cutters along with PDC cutters that were not subjected to the ion implantation were subjected to a non-instrumented drop weight impact tester to evaluate the cutters. This testing was done at the laboratories of GE Superabrasives in Columbus, Ohio. The test apparatus consisted of a 32.8Kg or 72 pound cylindrical steel weight attached on a vertical slide. The PDC cutter was attached to a fixture so that the cutting edge was positioned 20 degrees from a vertical axis of the steel weight. With a sacrificial hardened steel coupon resting on the cutter, the weight was dropped on the steel coupon from known heights. The results were that the ion implanted PDC diamond cutters had no damage after receiving 10 impacts from a height of 9cm, and 35 impacts from a height of 17cm. The number of impacts which normally cause the commercial PDC diamond cutter to chip and fracture is 10 or less from the 17cm height. These results are shown in the following Table 1:

DROP WEIGHT TEST - 32.8 Kg (72 lb)				
	Conventional PDC Diamond		Ion Implanted PDC Diamond	
HEIGHT	9cm (3.5 (inch)	17cm (6.75 inch)	9cm (3.5 inch	17cm (6.75 inch)
Number of Strikes	10	10	10	35
Diamond Damage	No	Yes	No	No

It should be noted that the commercial PDC diamond cutters, when subjected to the drop weight test, will show signs of chipping or fracture after being subjected to 10 or less hits from the 17cm drop height. Thus, in conducting the above test, the operator checked the diamond holding fixture for alignment after a total of 15 strikes from the 17cm drop height. The fixture was adjusted to be sure the diamond table was not supported by the fixture, and then 20 more strikes, for a total of 35, from the 17cm drop height were applied. The ion implanted PDC diamond cutter still had no abrasion, chipping or fracture.

From these tests, it is determined that the fracture toughness as well as the impact strength have been significantly increased over the comparable diamond tool which has not been subjected to the ion implantation. This will result in a greater number of parts being machined by the tool and/or a greater amount of drilling without replacing a drill bit using such diamond cutters. Therefore, the improvement extends the life of the cutter, which results in a great decrease in economic expenses in drilling, such as in the oil well or gas well field.

The durability of the diamonds can be improved by a stress relief which uses microwave heating. The microwave heating causes preferential heating of the trace elements and/or impurities of the diamonds, which appear in most of the manufactured diamonds, and act as dielectrics. Certain diamonds, such as TSP, which are free of cobalt, can be doped with dielectrics, such as silicon, silicon carbide and iron metals. The microwave heating for stress relief is a heating to a temperature below that which would destroy the particular diamond for a period of approximately five minutes. For example, the PDC and PCD diamonds are heated to a temperature of approximately 600°C at a slow rate, such as 30°C per minute, and held there for five minutes and then cooled at a slow rate, such as 30°C per minute. The other diamond-like materials, such as TSP, PVD diamonds, CVD diamonds, cubic boron nitride and cubic carbon nitride coatings, are heated to a temperature of approximately 900°C by the slow rate, such as 30°C per minute, and held for five minutes and then cooled at a slow rate, such as 30°C per minute.

The microwave heating causes the dielectric trace elements and impurities to soften or melt to heal micro-cracks. It should be pointed out that the ion implantation does not heal micro-cracks.

Therefore, if both microwave stress relief and ion implantation are to be done to the same diamond type, the implantation is done subsequent to any microwave stress relief.

As mentioned earlier, before any treatment is done, the diamond is tested or inspected by being subjected to microwave-induced stresses. Microwave-induced stresses are created by microwave heating at a rapid rate, such as 1000°C per minute, to the upper limit for the particular materials, such as around 600°C for PDC and PCD diamond materials and 900°C for TSP and other diamond-type materials, including the cubic carbon nitride coating and the cubic boron nitride materials and natural diamonds. Following the rapid heating, a rapid cooling occurs, and this creates stresses which, due to the thermal gradients within the diamond structure, will cause internal flaws and micro-cracks to propagate and rupture and fracture the material. Thus, the fractured or ruptured materials which have defects can be discarded. This is particularly useful when receiving a supply of diamond-type materials from a supplier and/or when utilizing used diamond-type materials.

It should be noted that microwave heating of these diamonds or diamond-like materials differs from the conventional heating, for example convective, inductive or other conventional heat treating methods. Microwaves preferentially heat only the dielectric trace and minor constituents.

Although various minor modifications may be suggested by those versed in the art, it should be understood that we wish to embody within the scope of the patent granted hereon all such modifications as reasonably and properly come within the scope of our contribution to the art.

WE CLAIM:

1. A tool comprising a diamond-like material having means for increasing the impact strength and fracture toughness of the material.

2. A tool according to claim 1, wherein the means for increasing impact strength and fracture toughness is an implantation of ions into the surface of the diamond-like material.

3. A tool according to claim 1, wherein the means for increasing the impact strength and fracture toughness is an ion implantation of at least one ion selected from the group consisting of aluminum, argon, boron, carbon, calcium, chromium, hydrogen, nitrogen, nickel, oxygen, ruthenium, silicon, tantalum, titanium, yttrium and zirconium.

4. A tool according to claim 3, wherein at least one of the ions is selected from a group consisting of chromium, nickel, ruthenium, tantalum, titanium and yttrium.

5. A tool according to claim 3, wherein the material is a thermally stable diamond compact.

6. A tool according to claim 5, wherein the thermally stable diamond compact is implanted with nickel and titanium ions.

7. A tool according to claim 3, wherein the material is a polycrystalline diamond compact on a cutter.

8. A tool according to claim 7, wherein the ions are nickel and titanium.

9. A process for improving the durability of a diamond-like material, said process comprising the steps of providing the material and treating the surface of the material to increase the impact strength and fracture toughness of the material.

10. A process according to claim 9, wherein the step of treating is by implanting ions into the surface of the material.

11. A process according to claim 10, wherein the step of implanting ions implants at least one ion selected from a group consisting of aluminum, argon, boron, carbon, calcium, chromium, hydrogen, nitrogen, nickel, oxygen, ruthenium, silicon, tantalum, titanium, yttrium and zirconium.

12. A process according to claim 11, wherein at least one of the ions is selected from a group consisting of chromium, nickel, ruthenium, tantalum, titanium and yttrium.

13. A process according to claim 11, wherein the step of providing the material provides a synthetic, thermally-stable diamond compact.

14. A process according to claim 13, wherein the step of implanting implants titanium and nickel ions.

15. A process according to claim 11, wherein the step of providing a material provides a polycrystalline diamond compact cutter.

16. A process according to claim 15, wherein the implanting occurs in a vacuum using titanium and nickel targets to create titanium and nickel ions.

17. A process for improving the durability of a diamond-like material comprising providing the diamond-like material having traces of dielectric material therein; slowly heating

the diamond-like material to an elevated temperature by microwave heating; holding at said elevated temperature for a period of time; and then cooling at a slow rate.

18. A process according to claim 17, wherein the step of providing a diamond-like material provides a material selected from a group consisting of cubic carbon nitride coatings, cubic boron nitride, thermally-stable diamond compact, plasma vapor-deposited diamonds, chemically vapor-deposited diamonds, single crystal natural diamonds and polycrystalline natural diamonds, said elevated temperature being approximately 900°C, said rate of slow heating and slow cooling being approximately 30°C per minute.

19. A process according to claim 17, wherein the diamond-like material is selected from a group consisting of polycrystalline diamond compacts and synthetic polycrystalline composite diamonds, said elevated temperature being approximately 600°C, and said slow rate of heating and cooling being approximately 30°C per minute.

20. A process for detecting defects in new and used diamond-like material, said process comprising rapidly microwave heating the diamond-like material at a rate of 1000°C per minute to a temperature below the temperature for destroying the diamond-like material, and then rapidly cooling the diamond-like material to create temperature gradients to accentuate fractures and flaws.

Fig 1

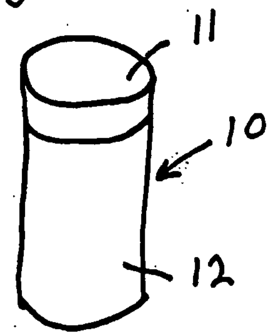


Fig 2

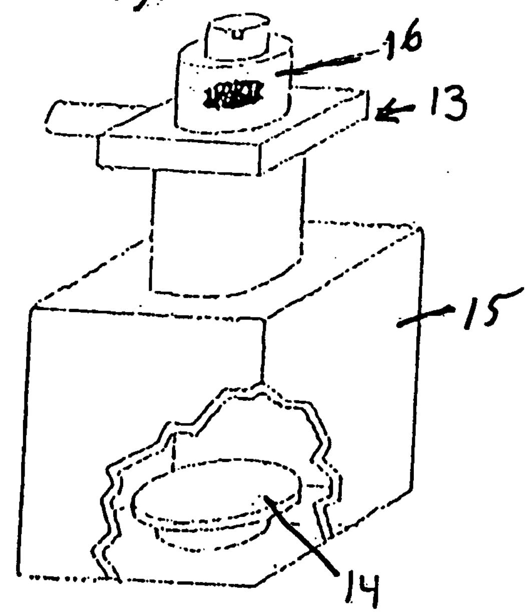


Fig 3